

# PATENT SPECIFICATION

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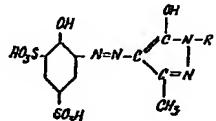
## COMPLETE SPECIFICATION.

### Manufacture of Metalliferous Monoazo-Dyestuffs

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which 5 we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides cobalt and 10 copper compounds of ortho-hydroxyazo-dyestuffs which contain two sulphonic acid groups and correspond to the formula

(1)



15 in which R represents a substituted or unsubstituted benzene radical free from sulphonic acid groups.

The new metal compounds can be obtained by treating a monoazo-dyestuff 20 containing two sulphonic acid groups and corresponding to the general formula (1) with an agent yielding cobalt or copper.

The metal-free monoazo-dyestuffs of the 25 general formula (1) are known. The method of making them from diazotised 2 - amino - 1 - hydroxybenzene - 4 : 6 - disulphonic acid and 1-phenyl-3-methyl-5-pyrazolones is also known. As 1-phenyl-3-methyl-5-pyrazolones there may be used 30 such compounds as 1-(4'-methylphenyl)-3-methyl-5-pyrazolone, preferably 1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone, 1-(3'- or 4'-chlorophenyl)-3-methyl-5-pyrazolone, 1-(2'-chlorophenyl)-3-methyl-5-pyrazolone and 1-phenyl-3-methyl-5-pyrazolone.

The conversion of the dyestuffs into 35 their copper and cobalt compounds can be carried out upon the crude products in the form in which they are present in the coupling mixture. Alternatively, the dye-

stuff may first be filtered off or purified, for example, by recrystallisation or by dissolving it and precipitating it from 45 solution.

The agents yielding cobalt or copper are preferably used in the form of salts which contain the metal as a cation, such, for example, as cobalt acetate, cobalt sulphate, copper sulphate or copper 50 acetate. In many cases it is of advantage to use complex metal compounds, for example, in the form of metal-ammine complexes, such as a copper tetrammine sulphate derived from ammonia, pyridine 55 or monoethanolamine, or in the form of compounds which contain one of the said metals in complex union in the anion, for example, complex cobalt or copper 60 compounds of alkali salts of aliphatic amino-carboxylic acids or of alkali salts of aliphatic amino-carboxylic acids or of alkali salts of aliphatic hydroxy-carboxylic acids, such as of glycine, lactic acid, and especially tartaric acid, for 65 example, sodium copper tartrate.

The treatment with the agent yielding metal may be carried out by a known method, for example, by heating to a temperature between 50 and 120° C. in an 70 open vessel, for example, under reflux, or, if desired, in a closed vessel under pressure, the pH value depending on the nature of the metallizing process; for example, acid coppering with copper 75 sulphate, and alkaline coppering with a copper tetrammine sulphate. If desired, other substances, for example, alcohol may be added.

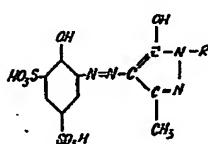
In metallizing the dyestuffs used as 80 starting materials in this invention, a rather short period of treatment at a temperature of 70 to 90° C. with salts, such as acetates or sulphates, may suffice.

The new metalliferous dyestuffs can be 85 worked up in the usual manner.

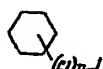
The new dyestuffs of the invention are complex copper or cobalt compounds containing the metal in complex union with

[Pri]

a monoazo-dyestuff of the general formula



in which R represents a substituted or unsubstituted benzene radical free from sulphonic acid groups. Especially valuable are the metal compounds of monoazo-dyestuffs of the above formula in which R represents a radical of the formula



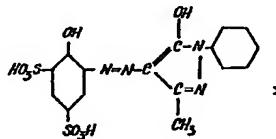
10 in which n represents a whole number which is at most 3.

The new complex copper and cobalt compounds are suitable for dyeing materials of animal origin. However, they 15 are especially suitable for dyeing anodically oxidised aluminium, on which they produce dyeings which are especially fast to light.

The following Examples illustrate the 20 invention, the parts and percentages being by weight:

#### EXAMPLE 1.

47.6 parts of the sodium salt of the dyestuff from diazotised 2-amino-1-hydroxybenzene-4:6-disulphonic acid and 1-phenyl-3-methyl-5-pyrazolone, which dyestuff corresponds to the formula



30 are dissolved at 70-75° C. in 150 parts of water and to the resulting solution there are added 120 parts of a copper sulphate solution containing 7.8 parts of copper. The whole is stirred at 70-75° C. for 30 minutes, and the completely precipitated complex copper compound is then separated by filtration. The cupriferous dyestuff so obtained is mixed with 40 parts of water and 30 parts of a sodium hydroxide solution of 30 per cent. 40 strength, and the resulting paste is dried under reduced pressure. The cupriferous dyestuff obtained in this manner is a yellow-brown powder which dissolves readily in water with a yellow-brown

coloration and dyes anodized aluminium 45 golden yellow tints of very good fastness to light.

For dyeing anodized aluminium the new dyestuff can be used as follows:

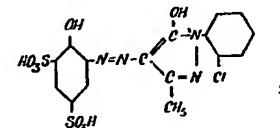
A piece of pure aluminium, which has 50 been anodically oxidised in the usual manner in a sulphuric acid electrolyte at a current density of 1.5 amperes per square decimeter, is treated for half an hour at 65° C. in a dye bath containing 55 0.05 to 0.2 gram per litre of the dyestuff. A brilliant golden tint is obtained which has an excellent fastness to light, after the usual sealing operation in boiling water.

The affinity of the dyestuff can be 60 increased by adjusting the pH value of the dye bath to 5 by the addition of, for example, 10 grams per litre of crystalline sodium acetate and 1 cc. per litre of acetic acid of 40 per cent. strength. 65

A similar copper compound is obtained by using 1-(4'-chloro)-phenyl-3-methyl-5-pyrazolone or 1-(2':5'-dichloro)-phenyl-3-methyl-5-pyrazolone, instead of 1-phenyl-3-methyl-5-pyrazolone in the 70 above Example.

#### EXAMPLE 2.

51 parts of the sodium salt of the dyestuff from diazotised 2-amino-1-hydroxybenzene-4:6-disulphonic acid and 1-(2':5'-chlorophenyl)-3-methyl-5-pyrazolone, which dyestuff corresponds to the formula



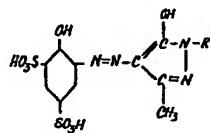
are stirred with 20 parts of crystalline sodium acetate in 500 parts of water and 80 dissolved by heating to 70° C. 120 parts of a cobalt sulphate solution containing 7.1 parts of cobalt are added, and the whole is stirred for 30 minutes at 70 to 75° C. The complex cobalt compound is 85 precipitated by the addition of 140 parts of sodium chloride, filtered off and dried. It is a brown powder which dissolves readily in water with an orange coloration and dyes anodized aluminium golden 90 yellow tints.

A similar complex cobalt compound is obtained in this manner by using the sodium salt of the dyestuff from diazotised 2-amino-1-hydroxybenzene-4:6-disulphonic acid and 1-phenyl-3-methyl-5-pyrazolone as starting material. 95

What we claim is:—

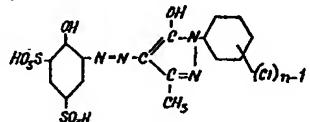
1. A process for the manufacture of monoazo-dyestuffs containing cobalt or 100

copper in complex union, wherein a monoazo-dyestuff of the general formula



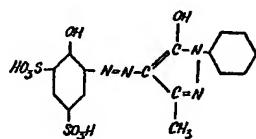
5 in which R represents a benzene radical free from sulphonate acid groups, is treated with an agent yielding cobalt or copper.

2. A process as claimed in claim 1, wherein there is used a monoazo-dyestuff 10 of the formula



in which n represents a whole number which is at most 3.

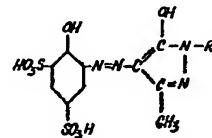
3. A process as claimed in claim 1, 15 wherein there is used the monoazo-dyestuff of the formula



4. A process for the manufacture of a 20 monoazo-dyestuff containing copper in complex union, conducted substantially as described in Example 1 herein.

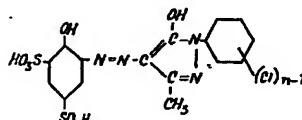
5. A process for the manufacture of a monoazo-dyestuff containing cobalt in complex union, conducted substantially 25 as described in Example 2 herein.

6. A complex cobalt or copper compound of a monoazo-dyestuff of the general formula



in which R represents a benzene radical 30 free from sulphonate acid groups.

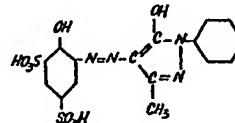
7. A complex cobalt or copper compound of a monoazo-dyestuff of the general formula



35

in which n represents a whole number which is at most 3.

8. A complex cobalt or copper compound of the monoazo-dyestuff of the formula 40



9. Any one of the complex metal compounds obtainable as described in Examples 1 and 2 herein.

10. A process for dyeing anodically 45 oxidised aluminium in which a complex cobalt or copper compound claimed in any one of claims 6 to 9 is used.

11. A process of dyeing anodically oxidised aluminium conducted substantially as described in Example 1 herein.

12. Anodically oxidised aluminium which has been dyed by the process claimed in claim 10 or 11.

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